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(54) **Production of gaseous olefins by catalytic conversion of hydrocarbons.**

(57) Various fractions of petroleum, including residual oils and crude oils, are catalytically converted to produce gaseous olefins, especially propylene and butylene, in fluidized or moving bed reactors with solid acidic catalysts in the presence of steam at a temperature of 500 °C to 650 °C and a pressure of  $1.5 \times 10^5$  Pa to  $3 \times 10^5$  Pa, with a weight space velocity of 0.2 to 20 hr<sup>-1</sup> and a catalyst-to-oil ratio of 2 to 12. Spent catalyst is continuously removed from the reactor to a regenerator where the coke is burned off and then the hot catalyst returned to the reactor. Comparing with the conventional catalytic cracking and tubular furnace pyrolysis process, the present invention produces more propylene and butylene, their total yield is about 40 per cent by weight of the feedstock.

**EP 0 305 720 A2**

# Production of Gaseous Olefins by Catalytic Conversion of Hydrocarbons

The present invention relates in general to the production of gaseous olefins, and most particularly to the production of propylene and butylene from petroleum hydrocarbons by catalytic conversion in which solid acidic catalysts are used.

Ethylene, propylene and butylene are produced conventionally from petroleum hydrocarbons such as natural gas, naphtha or light gas oil by well known tubular furnace pyrolysis. They are also produced from heavy petroleum fractions by pyrolysis over heat carrier or by catalytic of lower aliphatic alcohols. In modern refineries, gasoline and light gas oil are produced by conventional catalytic cracking, together with gaseous olefins as by-products at the yield of only less than 15 per cent by weight of the feedstock.

Recently, investigations for catalysts more effective to convert petroleum hydrocarbons to gaseous olefins have been reported from various patents. USP 3,541,179 discloses a fluidized catalytic cracking process for producing gaseous olefins. The catalysts include copper, manganese, chromium, vanadium, zinc, silver, cadmium or their mixtures deposited on alumina or silica. USP 3,647,682 discloses the preparation of lower olefins from butane or middle distillate by catalytic cracking over Y type zeolitic molecular sieves. More recent patents in the same area include DD 152, 356 which describes a method to produce C<sub>2</sub> to C<sub>4</sub> olefins from gasoline or vacuum gas oil by fixed or moving bed catalytic cracking over amorphous silica-alumina catalysts at a temperature of 600 to 800° C and for 0.3 to 0.7 seconds of contact time, with yields of 13.5% for ethylene, 6.3% for propylene and 10.5% for butylene. JP 60-222,428 discloses a process using the well known zeolite ZSM-5 as a catalyst and C<sub>5</sub> to C<sub>25</sub> paraffinic hydrocarbons as feed stock. The process is carried out at the reaction temperature of 600 to 750° C and a space velocity of 20 to 300 per hour, giving 30 per cent yield for C<sub>2</sub> to C<sub>4</sub> olefins. When naphtha is used, the yields of ethylene, propylene, and butylene are 16, 14, and 1.8 per cent, respectively. These processes reported above involve high cracking temperature, stringent requirement for material of cracking apparatus, hydrocarbons feed limited by a relatively narrow boiling range. And most processes aim at higher production of ethylene.

The object of the present invention is to overcome the disadvantages related in the prior art and provide a catalytic cracking process for the preparation of propylene and butylene with by-product distillate oils. Other objects and advantages will become apparent in the following detailed description.

In the process of the present invention, hydrocarbon feedstock is contacted with heated solid acidic catalysts in fluidized or moving bed or transfer line reactor and catalytically cracked, then the reaction products and spent catalysts are withdrawn from the reactor. After stripping and separating from reaction products, the spent catalyst deposited with coke is transferred to a regenerator where it contacts with oxygen containing gas at a high temperature and is regenerated by burning the coke deposited on the catalyst, and then returned to the reactor. By separation from the reaction products, C<sub>2</sub> to C<sub>4</sub> olefins, distillate oils, heavy oil and other saturated low hydrocarbons are obtained.

According to present invention preheated hydrocarbon feedstock is cracked over heated catalyst in the reactor at the temperatures from 500° C to 650° C, preferably from 550° C to 620° C. The weight hourly space velocity of the charge may range from about 0.2 to 20 hr<sup>-1</sup>, preferably from about 1 to about 10 hr<sup>-1</sup>. The catalysts-to-oil ratio may vary from 2 to 12, preferably from 5 to 10. In order to lower the partial pressure of hydrocarbon feed, steam or other gases, such as dry gas of catalytic cracking unit, may be added in the reactor during the conversion process. When steam is used, weight ratio of steam to hydrocarbon feed maintains at about 0.01 to about 2:1. The total pressure of the reaction is from 1.5 x 10<sup>5</sup> Pa to 3 x 10<sup>5</sup> Pa, preferably from 1.5 x 10<sup>5</sup> Pa. to 2 x 10<sup>5</sup> Pa. The obtained gaseous products may be separated into ethylene, propylene, butylene, and other components by using conventional techniques. Distilled liquid products include naphtha, light gas oil heavy gas oil and decanted oil. By further separation, benzene, toluene, xylenes, heavy aromatics, naphthalene, and methyl naphthalenes are obtained.

After reaction, spent catalyst is stripped and those hydrocarbons adsorbed on the catalyst are stripped out by steam or other gases. The spent catalyst deposited with coke thereon then is transferred to the regeneration zone. Regeneration is conducted by contacting the catalyst with oxygen-containing gas at a temperature of 650° C to 750° C. Afterwards the regenerated catalyst is returned to the reaction zone and used again.

Hydrocarbon feedstocks in accordance with this invention, which may vary in a wide range, comprise petroleum fractions with different boiling ranges, such as naphtha, distillates, vacuum gas oil, residual oil and the mixture thereof. Crude oil may also be used directly.

Catalysts used in the present invention are solid acidic catalysts comprising one or more active components and a matrix material. The active components includes amorphous aluminosilicate or zeolites

such as pentasil shape selective molecular sieves, faujasite, rare earth cation exchanged faujasite, chemically treated and/or stabilized faujasite and mixtures thereof. The matrix material includes synthetic inorganic oxides and mineral clays. All these catalysts are commercially available. Following table lists the trade names and some properties of these catalysts.

Catalyst in examples	Trade name	Al <sub>2</sub> O <sub>3</sub> %	Na <sub>2</sub> O %	Fe <sub>2</sub> O <sub>3</sub> %	Ignition loss, %	Attrition index, %
A	CHO	>48	<0.30	<0.90	<15	<2.0
B	ZCO	28	0.25	0.40	-	<2.0
C	CHP	50	<0.30	<0.90	<15	<3.0
D	mixture of B & C (1:1)	-	-	-	-	-
E	LWC II	>12	<0.05	<0.13	<13	<2.6

In the table, CHO is pentasil shape selective molecular sieves and rare earth exchanged Y sieves (REY) containing catalyst, ZCO is ultrastable hydrogen Y sieves (USY) containing catalysts, CHP is pentasil shape selective molecular sieves supported on kaolinite and LWC II is amorphous aluminosilicate catalyst. CHO, ZCO and CHP are manufactured by Catalyst Works of Qilu Petrochemical Company, SINOPEC. LWC II is manufactured by Catalyst Works of Lanzhou Refinery, SINOPEC. According to the present invention, use of the catalysts results in higher yields for gaseous olefins, especially propylene and butylene, by enhancing secondary cracking reaction, reducing hydrogen transfer reaction and prolonging contact time between hydrocarbon feed and catalysts.

The reaction temperature of the present invention is lower than that of prior catalytic conversion for producing gaseous olefins. Therefore expensive alloy steel material for the apparatus is not necessary. Besides, operating conditions and catalysts used in the present invention are properly selected so that selective cracking of hydrocarbon feed for production of olefins is enhanced but the formation of coke is reduced.

Comparing with the conventional catalytic cracking processes, the process of use present invention gives higher yield of gaseous olefins, especially propylene and butylene.

It is also possible to use the process of the present invention in the established fluidized catalytic cracking units by necessary modifications.

The following examples will serve to further illustrate this invention. These examples are to be considered illustrative only, and are not to be construed as limiting the scope of this invention.

#### Example 1.

This example illustrates the cracking of hydrocarbons by contacting them with different solid acidic catalysts.

Vacuum gas oil boiling from 350 °C to 540 °C with specific gravity 0.8730 was catalytically cracked on bench-scale fluidized cracking unit. The reactions were conducted at 580 °C, weight hourly space velocity of 1, catalyst to oil ratio of 5, and steam to hydrocarbon ratio of 0.3. From the results shown in Table 1, the yields of gaseous olefins over catalysts C and D are higher than the others.

Table 1

Catalysts	A	B	C	D
yields, wt% (based on the feed oil)				
Cracked gas	52.0	51.2	54.0	55.6
ethylene	3.04	3.19	5.89	5.23
propylene	15.52	17.39	21.56	21.61
butylene	15.64	14.47	15.64	15.09
C <sub>5</sub> -205 °C fraction	31.0	33.1	27.0	27.5
205-330 °C fraction	5.2	6.4	6.8	7.0
>330 °C	1.5	3.3	5.6	3.9
Coke	10.3	6.0	6.6	6.0
Conversion, wt%*	93.3	90.3	87.6	89.1
Ethylene + propylene + butylene, wt%	30.17	35.05	43.09	41.93
the catalysts A,B,C,D are being defined in the table of page 5.				

\*Note: conversion is calculated in terms of cracked gas, gasoline, coke and the loss (wt%)

### Example 2

This example illustrates the cracking of hydrocarbons under reaction temperature of 580 ° and 618 °C. Hydrocarbon feed is the same vacuum gas oil as in Example 1, but the test was carried out on a dense phase transfer line reactor pilot plant. The spent catalyst was transported into a generator where coke was burned with air in a dense phase fluid bed. Catalyst C was used in this test. A small amount of nitrogen instead of steam was added to promote the atomization of hydrocarbon feed. A small increase of gaseous olefins obtained at 618 °C is shown in Table 2, but a slight decrease of liquid yield is also observed.

Table 2

5	Reaction temperature, °C	580	618
	Weight hourly space velocity	3.9	4.1
	Catalyst to oil ratio	9.4	8.5
	Product yield, wt%		
10	Cracked gas	55.92	59.7
	Hydrogen	0.56	
	Methane	2.04	
15	Ethane	1.10	
	Ethylene	6.0	7.37
	Propane	2.37	
	Propylene	24.6	26.34
20	Propyne	0.16	
	i-Butane	1.66	
	n-Butane	0.87	
25	1-Butylene	2.94	} 17.0
	i-Butylene	6.44	
	t-2-Butylene	4.03	
	c-2-Butylene	3.04	
30	1,3-Butadiene	0.11	

to be continued--

Table 2 (continued)

35	C <sub>5</sub> -205°C fraction	22.38	19.5
	205-330°C fraction	7.3	6.8
40	>330°C	7.4	6.3
	Coke	5.9	7.1
	Loss	1.1	0.6
45	Ethylene+Propylene+Butylene, wt%	47.16	50.71

Compositions and octane number of C<sub>5</sub>-205°C gasoline fraction, obtained under reaction temperature of 580°C, are shown in Table 3.

Table 3

5		wt% in gasoline fraction
	Saturated hydrocarbons	10.64
	Olefinic hydrocarbons	38.90
	Aromatic hydrocarbons	50.46
10	Benzene	3.37
	Toluene	12.14
	Ethyl benzene	2.16
	m-,p-Xylene	11.00
	o-Xylene	3.39
15	m-, p-methyl -ethyl-benzene	1.58
	1,3,5-Trimethyl-benzene	0.77
	o-Methyl-ethyl-benzene	5.57
	1,3,4-Trimethyl-benzene	6.79
	other heavy aromatics	84.6
20	Octane number (motor method)	

Example 3.

This example illustrates that feedstocks with different boiling ranges can be used to produce gaseous olefins.

Table 4

30		Straight-run gasoline	straight run light gas oil	Vacuum gas oil	vacuum gas oil blended with equivalent residual oil
35	Specific gravity of Feedstock	-	0.8098	0.873	0.8823
	boiling range, °C	-	210-330	350-540	-
	Catalyst	E	D	D	D
	Apparatus of reaction	bench scale fluidized bed			
	Weight hourly space velocity	1.0	0.7	1.0	1.1
40	Reaction temperature, °C	650	580	580	580
	Product yield, wt%				
	Cracked gas	49.5	38.71	55.20	52.50
45	Ethylene	9.5	4.13	4.52	4.49
	Propylene	13.3	14.01	21.31	20.34
	Butylene	7.4	8.98	15.90	15.20
	C <sub>5</sub> -205 °C fraction	44.9	30.06	29.00	28.08
	205-330 °C fraction	--	27.50	5.60	6.70
	>330 °C	--	1.48	5.18	5.28
50	Coke	5.6	2.25	5.02	7.44
	Conversion, wt%	--	71.02	89.22	88.02
	Ethylene + propylene + butylene, wt%	30.2	27.10	41.73	40.03

Example 4.

This example illustrates that distillates derived from various crude oils can be used as feedstock in the process of this invention. By using catalyst C, the reaction was carried out at the temperature of 580 °C on a dense phase transfer line reactor as in Example 2. Results listed in Table 5 show that when vacuum gas oil (VGO) derived from paraffinic crude is used, the olefin yield is higher than that derived from intermediate base crude.

Table 5

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	VGO paraffinic crude	VGO intermediate base crude
Feedstock, specific gravity	0.873	0.8655
boiling range °C	350-450	210-480
UOP K Factor	12.4	12.1
Weight hourly space velocity	3.9	3.4
Product yield, wt%		
Cracked gas	55.92	47.55
Ethylene	6.00	5.30
Propylene	24.76	21.26
Butylene	16.56	14.21
C <sub>5</sub> -205 °C fraction	22.38	18.75
205-330 °C fraction	7.30	15.80
>330 °C	7.40	10.0
Coke	5.90	7.6
Conversion, wt%	85.3	74.2
Ethylene + propylene + butylene, wt%	47.32	40.77

35 Example 5

This example illustrates that crude oil can be used as feedstock directly in the process of the present invention.

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Table 6

	Paraffinic crude oil
Specific gravity of feedstock	0.862
Catalyst used	D
Reaction apparatus	bench-scale fluidized bed
Weight hourly space velocity	1.0
Reaction temperature, °C	580
Product yield, wt%	
Cracked gas	46.6
Ethylene	4.3
Propylene	17.8
Butylene	12.7
C <sub>5</sub> -205 °C fraction	31.2
205-330 °C fraction	10.4
>330 °C	3.5
Coke	8.3
Ethylene + propylene + butylene, wt%	34.8

Example 6

This example illustrates that product yield is varied with different reaction temperature, space velocity, and the amount of steam injected. VGO feedstock is the same as in Example 1. A bench-scale fixed fluidized catalytic cracking unit and catalyst D are used.

Table 7

Reaction temperature, °C	540	580	600
Weight hourly space velocity	0.5	1.1	19
Amount of steam/oil, wt.	0.55	1.88	0.02
Product yield, wt%			
Cracked gas	52.8	56.1	44.6
Ethylene	4.2	4.3	3.2
Propylene	19.9	24.6	16.9
Butylene	14.7	18.7	14.1
C <sub>5</sub> 205 °C fraction	29.7	29.0	32.3
205-330 °C fraction	6.9	6.2	10.0
>330 °C	4.7	5.3	8.9
Coke	5.9	3.4	4.2
Conversion, wt%	88.4	88.5	81.1
Ethylene + propylene + butylene, wt%	38.8	47.6	34.2

**Claims**

1. A process for preparing gaseous olefins by catalytic conversion which comprises contacting petroleum hydrocarbon feedstock under cracking conditions with a catalyst, characterized in that said feedstock is contacted with solid acidic catalyst in a fluidized or moving bed or transfer line reactor in the



presence of steam at a temperature of 500° C. to 650° C and a pressure between  $1.5 \times 10^5$  Pa. and  $3.0 \times 10^5$  pa. with a weight space velocity of 0.2 to 20 hr<sup>-1</sup>, a catalyst-to-oil ratio of 2 to 12, and steam-to-feed ratio of 0.01 to 2:1 by weight, to carry out the cracking reaction.

2. A process of claim 1 wherein

5 said solid acidic catalyst comprises amorphous aluminosilicate or synthetic zeolites selected from the group consisting of pentasil shape selective molecular sieves, faujasite, rare earth cation exchanged faujasite, chemically treated and/or stabilized faujasite and mixtures thereof as active components and matrix material selected from synthetic inorganic oxides, mineral clays and mixtures thereof.

3. A process of claim 1 or 2 wherein said solid acidic catalyst preferably comprises pentasile shape  
10 selective molecular sieves and/or USY(ultra stable hydrogen y) zeolites.

4. A process of claim 2 wherein said solid acidic catalyst preferably comprises matrix material selected from amorphous silica-alumina, aluminium oxide and kaolin clay.

5. A process of any of the preceding claims wherein said hydrocarbon feedstock comprises oil distillates selected from gasoline, kerosene, gas oil, residual oil and mixtures thereof or crude oil.

15 6. A process of claim 5 wherein said hydrocarbon feedstock is preferably selected from vacuum gas oil or atmospheric residual oil derived from paraffinic base crude oil.

7. A process of any of the preceding claims wherein dry gas or other gases is added to the reactor during the cracking reaction.

8. A process of claim 7 wherein the steam-to-feedstock ratio is preferably 0.05 to 1:1 by weight when  
20 steam is added.

9. A process of any of the preceding claims wherein the cracking reaction is preferably carried out at a temperature in the range of 550° C. to 620° C., pressure in the range of  $1.5 \times 10^5$  Pa. to  $2.0 \times 10^5$  Pa. and a weight space velocity of 1 to 10 hr<sup>-1</sup>.

10. A process of any of the preceding claims wherein the spent catalyst after reaction is stripped,  
25 regenerated at a temperature of 650° C to 750° C in the presence of oxygen-containing gas and then returned in hot state to the reactor for reuse.

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